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CHEMICAL/BIOLOGICAL RELATIONSHIPS RELEVANT TO ECOLOGICAL EFFECTS OF ACID RAINFALL

John O. Reuss

National Ecological Research Laboratory
Corvallis, Oregon

June 1975

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Chemical/Biological Relationships Relevant to Ecological Effects of Acid Rainfall

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The theory of the carbon dioxide-bicarbonate equilibria and its effect on rainfall acidity is given. The relationship of a cation-anion balance model of acidity in rainfall to plant nutrient uptake processes is discussed, along with its relationship to a model previously proposed in the literature. Average H^+ concentration calculated from pH measurements does not appear to be a satisfactory method of determining H^+ loading from rainfall if the rain is not consistently acid. Calculating loading from H^+ minus HCO_3^-, strong acid anions minus basic cations, or net titratable acidity is suggested.

The flux of H^+ ions due to plant uptake processes and sulfur and nitrogen cycling is considered. H^+ is produced by oxidation of reduced sulfur and nitrogen compounds mineralized during decomposition of organic matter. Plant uptake processes may result in production of either H^+ or OH^- ions. Fluxes of H^+ from these processes are much greater than rainfall H^+ inputs, complicating measurement and interpretation of rainfall effects. The soil acidifying potential due to the oxidation of the NH_4^+ in rainfall is apparently of a similar magnitude to the direct acidity inputs.

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ABSTRACT

This paper deals with problems concerning measurements of rainfall acidity and interpretation in terms of possible effects on the soil-plant system.

The theory of acidity relationships of the carbon dioxide-bicarbonate equilibria and its effect on rainfall acidity measurements is given. The relationship of a cation-anion balance model of acidity in rainfall to plant nutrient uptake processes is discussed, along with the relationship of this model to a rainfall acidity model previously proposed in the literature. These considerations lead to the conclusion that average H^+ concentration calculated from pH measurements is not a satisfactory method of determining H^+ loading from rainfall if the rain is not consistently acid. Calculating loading from H^+ minus HCO_3^-, strong acid anions minus basic cations, or net titratable acidity is suggested.

The flux of H^+ ions in soil systems due to plant uptake processes and sulfur and nitrogen cycling is considered. H^+ is produced by oxidation of reduced sulfur and nitrogen compounds mineralized during decomposition of organic matter. Plant uptake processes may result in production of either H^+ or OH^- ions. Fluxes of H^+ from these processes are much greater than rainfall H^+ inputs, complicating measurement and interpretation of rainfall effects. The soil acidifying potential due to the oxidation of the NH_4^+ in rainfall is examined, with the conclusion that acidity from this source is of a similar magnitude to direct H^+ inputs common in rainfall.

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SECTION I

CONCLUSIONS

A number of chemical and biological considerations relevant to understanding the effects of rainfall acidity on soil-plant systems have been discussed. The following points are particularly important and should be thoroughly understood by researchers engaged in acid rainfall investigations:

1. Hydrogen ion inputs from rainfall to soil and aquatic systems calculated from "weighted average" pH measurements without regard to bicarbonate levels or carbon dioxide partial pressures may be seriously in error. Alternative methods include; H^+ minus HCO^-_3, net titratable acidity, and acid anions minus basic cations.

2. The potential of rainfall to acidify soil or waters is characterized by its containing more acid anions than basic cations. This excess of anions can be an appropriate measure of the capacity of the rainfall to contribute to the acidity of soil-water systems.

3. The acidity of a plant growth medium is affected by the relative uptake of cations and anions by the plants growing in the medium. The overall effect of acid rainfall is not only the effect of H^+ ions added to the system but may also reflect the relative plant uptake of the various ions added to the system.

4. In the natural sulfur cycle, H^+ ions are continually being formed and consumed by various biological processes. An important aspect of the acid rainfall question involves the effect of additional sulfur loading on these processes.

5. Soil nitrogen transformations normally involve a substantial production and consumption of H^+ ions. This flux of H^+ ions is much larger than that involved in sulfur transformation or the input from acid rainfall. Measurement of the effects of H^+ inputs from outside the system may be complicated by this larger flux due to normal nitrogen transformations.

6. The oxidation of ammonium to nitrate by aerobic chemautotrophic bacteria results in the production of acid. Oxidation of the ammonium contained in rainfall may result in an H^+ production of a similar order of magnitude to the direct input of H^+ in acid rain. The consideration of this process substantially complicates the interpretation of rainfall induced H^+ loading.

SECTION II

RECOMMENDATIONS

1. Hydrogen ion concentrations (pH) measurements on rainfall should normally be made after equilibration with known CO_2 partial pressures, preferably the standard atmospheric level (approximately 316 parts per million).

2. Net rainfall inputs of H^+ ion to soil and aquatic systems should not be calculated simply as the sum of the H^+ ions contained in the rainwater if pH values above 5.0 are encountered. Appropriate methods would include; H^+ minus HCO^-_3, acid anions minus basic cations, and net titratable acidity.

3. Reporting ions input to soil or aquatic systems on a weight per unit area basis is often misleading. Reporting on the basis of chemical equivalents per unit area is recommended.

4. Research should be conducted that will quantify the effect of rainfall acidity on soil systems. This should include the theoretical soil chemistry of low level chronic acid inputs on soils, applied measurements of acidification rates in laboratory and field systems, and methods of evaluating the interaction of acid inputs and plant systems on soil acidity.

5. In conjunction with (4) above systems models should be developed to simulate the long-term effects of rainfall acidity on soil and soil-plant systems.

6. The potential acidification resulting from NH^+_4 inputs should be considered in ecological investigations concerned with acid rainfall.

SECTION III

INTRODUCTION

Presently the phenomenon known as "acid rainfall" is arousing a great deal of interest. Evidence has been accumulated to support the assumption that in some areas the acidity of rainfall has been increasing in recent years as a result of man's activity. This increase has been assumed to be largely due to increased atmospheric inputs of SO_2 from anthropogenic sources (Likens, 1972; Likens and Bormann, 1974). Various investigators have called attention to possible adverse effects of the acidity on terrestrial and aquatic ecosystems.

Several important aspects of this problem may not have received adequate attention in the scientific literature. These include problems associated with collection, measurement, and reporting, as well as possible interactions of rainfall acidity with soil-plant processes such as the cycling of sulfur and nitrogen. The purpose of this paper is not to support or to contest the validity of the hypothesized adverse ecological effects due to acid rainfall. Rather, the information and concepts presented here are intended to be useful in the formulation of testable hypotheses and to provide a firmer basis for future experiments designed to measure these ecological effects.

SECTION IV

CARBON DIOXIDE-BIOCARBONATE EQUILIBRIUM IN RAINFALL

Various investigators have recognized the importance of the carbon dioxide-bicarbonate system in determining the pH of otherwise neutral rainwater (Barret and Brodin, 1955; Pearson and Fisher, 1971; Likens and Bormann, 1974). Unfortunately many of the reporting practices and interpretations found in the literature suggest that this system is not adequately taken into account. While a dissolution of $CaCO_3$ dust by acidic aerosols could certainly result in bicarbonate in the rainfall as suggested by Pearson and Fisher (1971), this mechanism is not necessary to account for the presence of the bicarbonate ion. Observed bicarbonate levels of rainfall are best understood by considering the equilibrium with atmospheric carbon dioxide. Perhaps a short explanation will be useful to workers concerned with rainwater chemistry and its ecological implications.

The generally accepted standard atmospheric CO_2 concentration is approximately 316 parts per million (ppm) or a partial pressure of 3.16×10^{-4} atmospheres. The reactions of CO_2 and water can be represented by (1) and (2) below and these are summed to obtain (3).

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \qquad (1)$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad (2)$$

$$CO_2 + H_2O \rightleftarrows H^+ + HCO_3^- \qquad (3)$$

The logarithms to the base 10 of the equilibrium constant K at 25°C for (1) and (2) are given by Sillen and Martell (1964) as -1.46 and -6.35 respectively. These are summed to obtain log K of -7.81 for (3), and the equilibrium expression is given by (4).

$$\frac{[H^+]\,[HCO_3^-]}{[CO_2]_g} = 10^{-7.81} \qquad (4)$$

The $[H^+]$ and $[HCO_3^-]$ are the ion activities in moles per liter and are considered to be identical to concentration in this very dilute system. The $[CO_2]_g$ refers to the partial pressure of CO_2 in atmospheres.

If we restrict the system to atmospheric CO_2, $[CO_2]_g$ becomes 3.16×10^{-4} and (4) can be rearranged as follows:

$$[H^+]\,[HCO_3^-] = (10^{-7.81})\,(3.16 \times 10^{-4})$$

from which we obtain Equation (5).

$$[H^+]\,[HCO_3^-] = 10^{-11.31} \qquad (5)$$

In a pure water system with CO_2 as the only source of HCO_3^- and assuming sufficient acidity to keep direct hydrolysis of water insignificant compared to the $[H^+]$ ion derived from the CO_2 equilibrium process, the $[H^+]$ concentration must equal $[HCO_3^-]$. Therefore, from (5) above, we can write:

$$[H^+]^2 = 10^{-11.31}$$

$$[H^+] = 10^{-5.65}$$

Thus, we expect a pH of 5.65 (and $pHCO_3$ of 5.65) for pure rainwater in equilibrium with atmospheric CO_2 at 25°C. The concentration of H^+ and HCO_3^- would be 2.2×10^{-6} moles per liter. With a rainfall of one meter annually, the "loading" would be 2.2×10^{-3} moles per square meter per year. Hydrogen ion loading values in this range are not meaningful as the concentrations within the soil system are controlled by the CO_2 partial pressure in the soil. If rainfall or soil solution is more acid than pH 5.65 for reasons other than the effect of CO_2, the $[H^+]$ term in Equation (5) increases and the $[HCO_3^-]$ decreases. Bicarbonate concentrations decrease to insignificant levels between pH 5 and 4, and in more acid systems CO_2 partial pressures become unimportant in controlling pH.

In basic or near neutral solutions in equilibrium with CO_2, the HCO_3^- ion is very important. From the dissociation of water at 25°C as shown in Equation (6), we obtain Equation (7).

$$[H^+]\,[OH] = 10^{-14} \tag{6}$$

$$[H^+] = \frac{10^{-14}}{[OH^-]} \tag{7}$$

Substituting (7) into (4) above we have:

$$\frac{\left[\frac{10^{-14}}{OH}\right]\,[HCO^-_3]}{(CO_2)_g} = 10^{-7.81}$$

Which can be rearranged to (8)

$$\frac{[HCO^-_3]}{[CO_2]_g\,[OH]} = 10^{6.19} \tag{8}$$

Equation (8) is the equilibrium expression for reaction (9):

$$CO_2 + OH^- \rightleftarrows HCO_3^- \qquad (9)$$

On further rearranging Eq. (8) we have Eq. (10):

$$\frac{[HCO_3^-]}{[OH^-]} = 10^{6.19}[CO_2]_g \qquad (10)$$

which at atmospheric CO_2 concentration of 3.16×10^{-4} becomes:

$$\frac{[HCO_3^-]}{[OH^-]} = 490 \qquad (11)$$

Equation (11) states that the concentration of HCO_3^- in equilibrium with atmospheric CO_2 will be 490 times that of OH^-. This is a very important relationship and explains why we would not normally expect to encounter a "basic rain" phenomenon while acid rain is common. A likely source of basic alkaline earth cations in the atmosphere would be the burning of fuels high in these cations. These would enter the atmosphere as oxides--- i.e. CaO, Na_2O, MgO etc.---and, on encountering water droplets, would be hydrated to hydroxides. The hydroxides would be very basic if it were not for the presence of CO_2 in the atmosphere. However, the OH^- will be rapidly converted to HCO_3^- and, at equilibrium, 490 bicarbonate ions will be present for each hydroxyl. This provides an effective buffer and prevents highly alkaline conditions from occurring at the ionic concentrations found in rainfall.

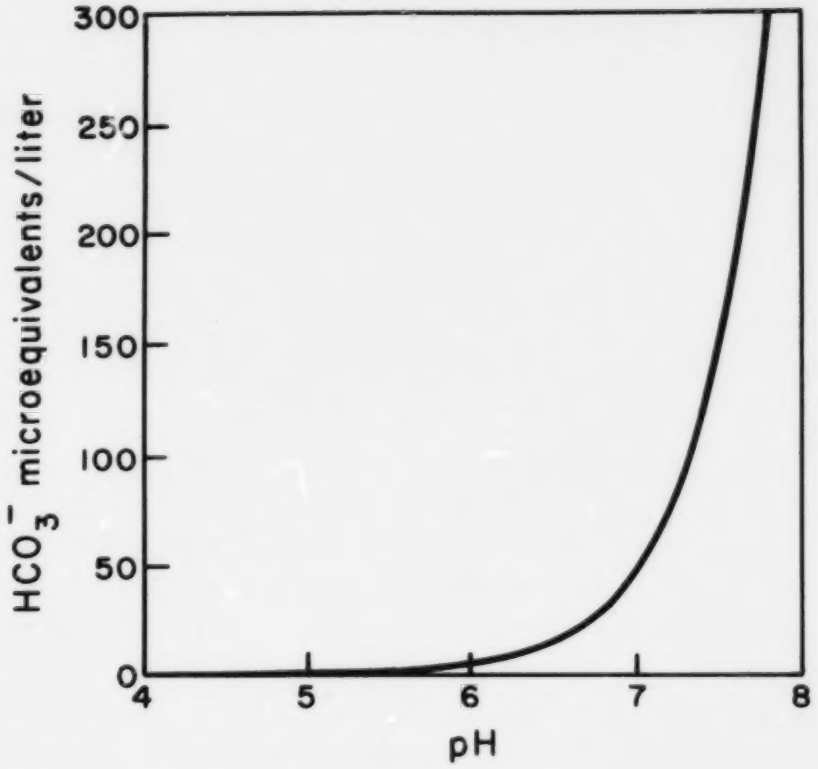

Figure 1 The relationship between pH and HCO_3^- activity in equilibrium with atmospheric CO_2 (316 ppm).

A convenient form of Equation (5) above is shown in (12):

$$[HCO_3^-] = 10^{pH-11.31} \quad (12)$$

Equation (12) shows clearly that, for a system in equilibrium with atmospheric CO_2 at any given pH, the HCO_3^- concentration is fixed or, conversely, for any HCO_3^- concentration the pH is fixed. If data are reported that do not fit this relationship the system probably was not in equilibrium with a CO_2 partial pressure of 3.16×10^{-4} atmospheres. The graphical presentation in figure 1 over the range usually encountered in rainfall samples shows clearly that alkaline rainfall could only occur in the presence of very high bicarbonate levels.

The above discussion ignores the carbonate ion. This need not concern us here, because the mole fraction of dissolved carbon in the CO_3^{2-} forms is negligible at the pH values considered. As pH increases, CO_3^{2-} increases. If pH values above about 8.5 were encountered, this ion would become significant.

The relevance of the bicarbonate-hydroxyl and bicarbonate-hydrogen ion equilibria becomes apparent when we consider the overall chemistry of atmospheric aerosols. As mentioned above, if bases enter the atmosphere from the burning of fossil fuels, particularly coal, they would be in the oxide form and would hydrate to the corresponding hydroxide. On further reacting with acid aerosols formed from SO_x and NO_x gases, they would be neutralized. If the acids exceed the bases, the rainfall will be acid, i.e., the anions will be present in larger amounts than the basic cations, and electrical neutrality will maintained by the presence of the H^+ ions. The rainfall pH will be below the 5.65 expected from CO_2 equilibrium, HCO_3^- will be very small as shown in figure 1, and the well-known acid rainfall phenomenon results.

If the basic cations exceed the anions, substantial quantities of HCO_3^- will be expected rather than high levels of OH^-. This result can be predicted from (11), as under equilibrium conditions the HCO_3^- will be 490 times as high as OH^-. In most cases the HCO_3^- ion may be regarded as the alkaline component of rainfall rather than the OH^- ion. When rainfall containing HCO_3^- enters an acid soil, the bicarbonate acts as a base, each HCO_3^- reacting with 1 H^+ ion to form CO_2 and H_2O as shown by the reverse of equation (3).

An interesting effect occurs if mean concentrations are calculated for two or more samplings. Barret and Brodin (1955) suggest calculating the H^+ concentration for each sample and multiplying by the measured sample volume. These are summed, divided by the total volume and the resultant concentration reconverted to a pH value. This is the usual method of calculating "average" pH values and H^+ ion loading. The implications are that this would be the pH of the total rainfall collected if all samples are mixed together. Unfortunately, if HCO_3^- was present in any of the samples this would not be the case, at least after equilibration with atmospheric CO_2.

Consider two samples, (a) at pH 7.0 and (b) at pH 5.0. At equilibrium with the atmosphere, the HCO_3^- concentrations would be 49.0 and 0.49 micromoles per liter for (a) and (b), respectively. If we calculate an average H^+ and HCO_3^- concentration by the above procedure for a mixture of equal volumes of (a) and (b), the calculated pH of the mixture is 5.30 and the HCO_3^- concentration is 24.7 micromoles per liter. This solution in actual practice would only be compatible with a CO_2 partial pressure of about 6000 ppm. If we physically mix (a) and (b) and allow it to equilibrate with the atmosphere, equal amounts of H^+ and HCO_3^- would react to form CO_2 and H_2O until the relationship shown in equation (4) was satisfied. The fact that the H^+ and HCO_3^- concentrations would decrease by equal amounts allows us to calculate the resultant pH and HCO_3^- as follows. Let:

$$X = \text{change in } HCO_3^- \text{ or } H^+$$

$$[H^+] = (10^{-5.30})-X$$

$$[HCO_3^-] = (24.7 \times 10^{-6})-X$$

By substituting these values into equation (5) and solving the resultant quadratic, we find that H^+ and HCO_3^- decrease by 4.8×10^{-6} moles per liter during equilibration. The final pH of the mixture would be 6.6, and the HCO_3^- concentration would be 19.9 micromoles per liter. This illustrates that if bicarbonates are present, the average pH as usually calculated would not be the same as the measured pH of composite samples.

The implications of this effect are important. Hydrogen ion loadings per unit area are normally calculated by the same procedure as is average H^+ concentration or pH. The above example shows that if two rainfall events are collected separately the calculated H^+ loadings may not be the same as if the two samples are allowed to accumulate in the collection device prior to analysis. Also if one event were divided into several successive sampling periods, and each period was analyzed separately, the average pH and H^+ loading observed would be different than that obtained if the collection accumulated throughout the event. The possible variations are endless and, in my opinion, indicate a fundamental error in the usual methods of analysis and interpretation.

Changes in CO_2 partial pressure during sample collection and storage could significantly affect pH and bicarbonate measurements on many rainwater samples. For illustration, Figure 2 plots the HCO_3^- and pH values for a series of rainwater samples reported by Egner and Eriksson (1955a, 1955b). The reported pH values are generally about 0.5

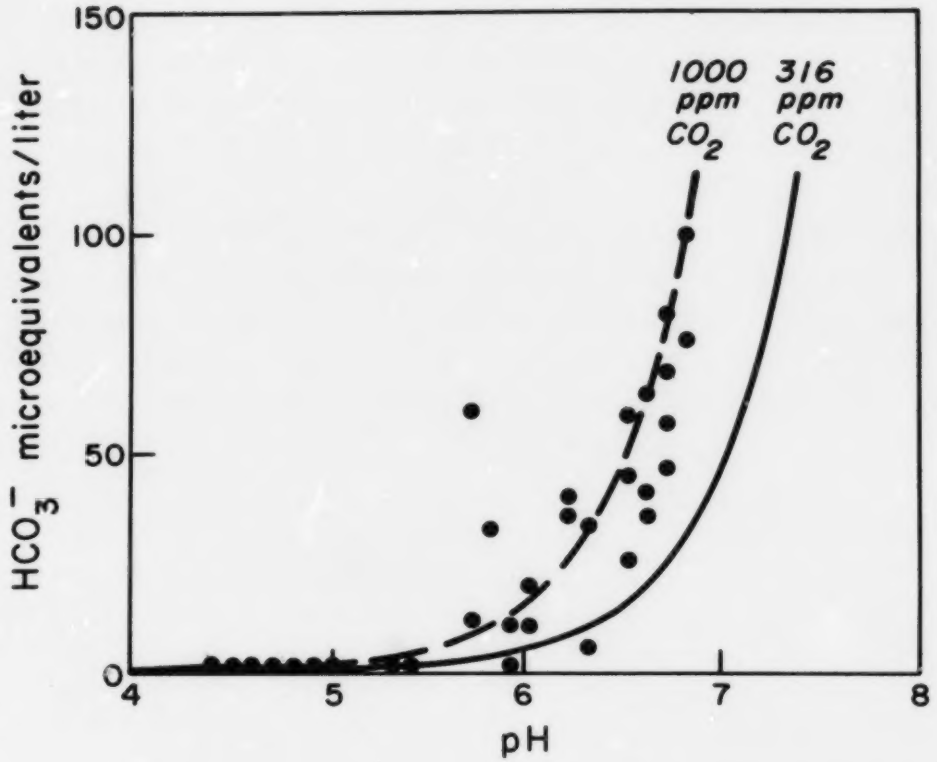

Figure 2 Plot of the pH and HCO_3^- levels reported by Egner and Eriksson (1955b, data set D501).

unit lower than would be consistent with a CO_2 concentration of 316 ppm but are generally much more consistent with 1000 ppm CO_2. The 1000 ppm level could easily exist in confined collection vessels or storage containers, but there is no way to be certain that this is the cause of the discrepancy. Granat (1972) has reported a similar and consistent effect in a large number of samples. He suggests the effect is due to the presence of undissolved materials that yield the major ions commonly found in rainfall upon dissolution, but Granat does not suggest any compounds with the necessary properties.

Even though problems of pH and acidity measurements in rainfall appear formidable, we must address the question of how best to proceed. In practice few errors will result from pH measurements at unknown CO_2 concentrations if the rainfall is consistently acid. However, if non-acidic events are interspersed with acid events, the errors could be substantial.

The diagram shown in Figure 3 should prove useful in this regard. It is developed by utilizing the principle that the net alkalinity b is independent of CO_2 partial pressure, and in systems where the CO_3^- ion is negligible, is defined by (13).

$$b = [OH^-] + [HCO_3^-] - [H^+] \qquad (13)$$

Rearranging (13):

$$[HCO_3^-] = b - [OH^-] + [H^+]$$

Substituting for $[HCO_3^-]$ in (4) above and replacing $[OH^-]$ by $\frac{10^{-14}}{[H^+]}$ we have:

$$\frac{[H^+]}{[CO_2]} \left(b + [H^+] - \frac{10^{-14}}{[H^+]}\right) = 10^{-7.81}$$

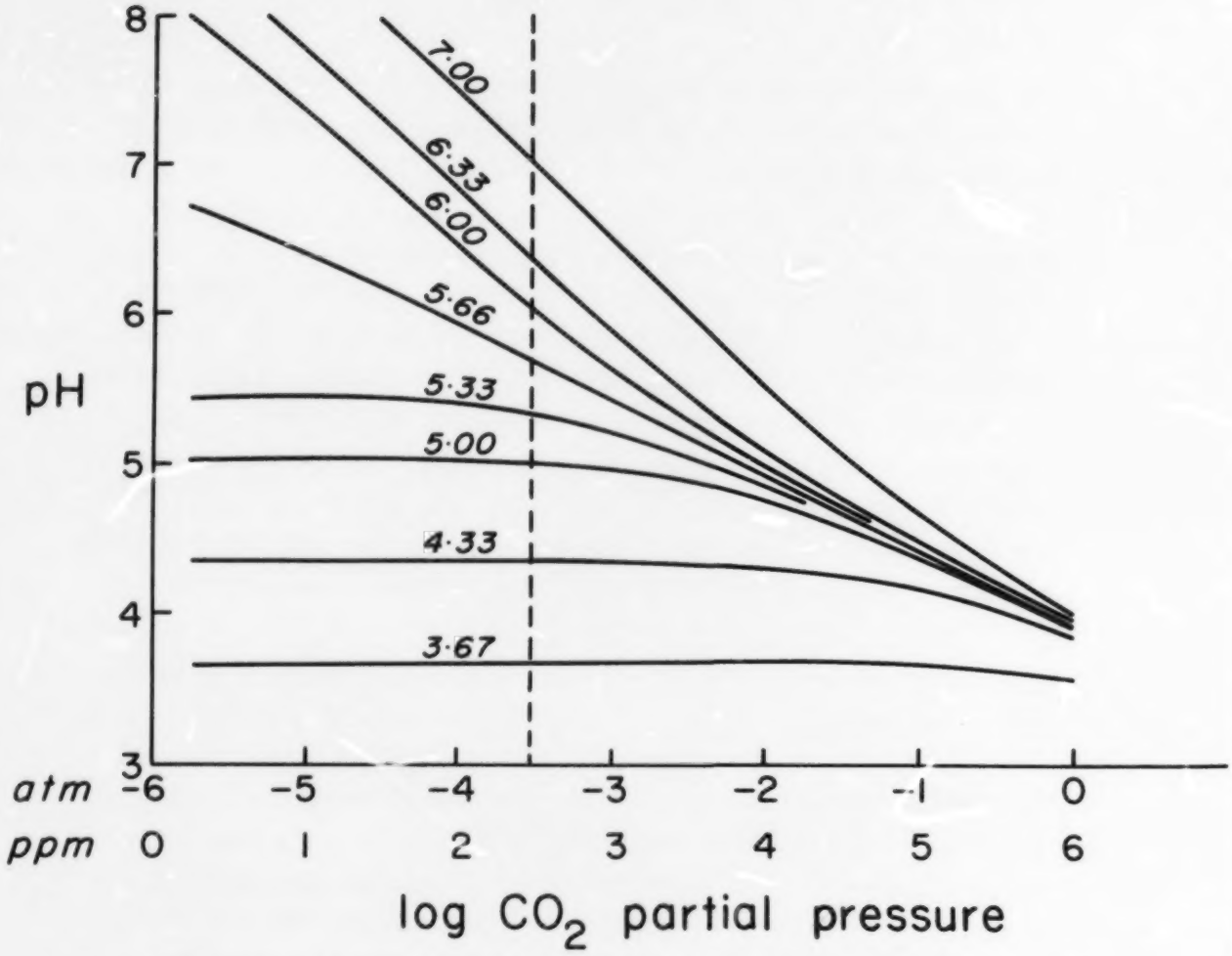

Figure 3 Diagram showing the effects of varying CO_2 partial pressure on pH. Dotted line indicates 316 ppm CO_2 and numbers refer to pH at 316 ppm CO_2.

which rearranges to (14).

$$[H^+]^2 + [H^+]b - 10^{-7.81}\,[CO_2] - 10^{-14} = 0 \qquad (14)$$

For any combination of pH and CO_2 partial pressure, $[OH^-]$ and $[HCO_3^-]$ may be calculated by means of (4) and (6) and b calculated from (13). To construct figure 3 arbitrary pH values were selected and the values of b determined for 316 ppm CO_2. The lines were then generated by calculating $[H^+]$ as a function of $[CO_2]$ using (14).

No significant effects due to CO_2 partial pressure variations would be expected where the lines on Figure 3 are horizontal. In general the CO_2 pressures of interest are in the range of 300 to 1000 ppm, but higher values may occur. From the graph we see that with samples below pH 4.33 no effects occur within the range of interest, but at pH 5.0 CO_2 pressures above 1000 ppm would depress measured pH. With samples above pH 5.00 the error due to variations in CO_2 becomes unacceptable.

Several methods might be employed to minimize possible errors. First, I suggest that reported pH values should be those taken only after equilibration with known CO_2 partial pressures, preferably about 316 ppm. This would assure uniformity between samples and provide a uniform basis for comparing data from different investigations. This equilibration is particularly important with samples above pH 5.0. Secondly, H^+ ion loadings per unit area should <u>not</u> be calculated by simply determining total H^+ from pH and volume measurements. The long-term effects on soil systems are more likely to be related to the net H^+ loading over time. This would be the difference between H^+ and titratable alkalinity or, in practical terms, H^+ minus HCO_3^-. The HCO_3^- represents the alkaline component of the rainfall so in order to

estimate net H^+ loading from pH measurement, the HCO_3^- must be subtracted from the total H^+ found. This method has been used by Granat (1972). Alternatively, titration methods could be used and H^+ loading calculated as the difference between titratable acidity and alkalinity. If all major cations and anions are determined, a method of calculating net acidification using anion-cation balances as discussed in the next section should be considered.

SECTION V

CATION-ANION BALANCE IN RELATION TO ACID RAINFALL

An important property of solution systems, whether soil solution or rainfall, is that electrical neutrality is maintained. The chemist analyzing precipitation or stream water utilizes this property when he checks his results to ascertain whether the cations found equal the anions. If the difference exceeds normal analytical uncertainty, either an analytical error has been made or some important constituent has not been determined.

This property may be utilized effectively in determining the acidity of rainfall in the absence of pH measurements, provided the major cations and anions have been accurately determined. Consider a rainfall system containing salts of strong acids and strong bases only. The pure water system would be approximately neutral and weakly buffered. In the presence of atmospheric CO_2, the concentration of H^+ and HCO_3^- ions would be approximately 2.6×10^{-6} moles per liter and the pH at 25°C would be 5.65 as shown in Section IV above.

The major anions other than HCO_3^- involved in the system are NO_3^-, Cl^-, and SO_4^-. Major cations commonly encountered are Ca^{2+}, Mg^{2+}, Na^+, K^+, and NH_4^+. If the anions exceed the cations, electrical neutrality of the system is maintained by H^+ ions and the system is acid. This is the situation we would expect when acidification occurs due to H_2SO_4 and HNO_3 formed from SO_x and NO_x gases in the atmosphere. Excluding HCO_3^- and H^+, the excess of anions over cations on an equivalent basis may be used to estimate net acidity as shown by (15).

$$e = 2\,[SO_4^{2-}] + [NO_3^-] + [Cl^-] - 2\,[Ca^{2+}] \\ -2\,[Mg^{2+}] - [K^+] - [NH_4^+] \qquad (15)$$

where: e = excess acid in moles per liter (-e = alkalinity).

For certain ecosystem effects this measurement may be more appropriate than direct H^+ measurements. For instance, the long-term effects of soil acidification are probably more appropriately considered in terms of a deficit of basic cations than in terms of H^+ ions directly. If the excess anions in acid rainfall are mobile, they will be leached from the soil in association with bases from the exchange complex, resulting in base depletion and acidification. Some soils, particularly those that are acid and highly weathered, exhibit significant anion exchange properties. In these soils anion mobility is reduced, and an excess of acid anions over basic cations may not result in base depletion. This condition is discussed more fully in relation to the sulfur system in the next section.

If the basic cations in rainfall exceed the anions, the deficit would be made up by OH^- ions in solution if no CO_2^- was present. In the atmosphere, the OH^- ions are rapidly converted to HCO_3^- as explained above. At any rate, the excess of basic cations over anions (excluding HCO_3^-) should be an appropriate measure of the ability of the rainwater to increase the base status of the lithosphere or hydrosphere.

In practice rainfall acidity measurements derived from anion minus cation calculation should correspond very closely to values obtained by substracting HCO_3^- from H^+ derived from pH measurements. Rainwater at pH 5.0 contains 10 micromoles H^+ per liter and 100 micromoles per liter at pH 4.0. Cation levels are generally of the same order of magnitude, so measurements that give acceptable accuracy of the cations and anions in this range should also combine to give acceptable estimates of net

acidity or alkalinity. Occasionally rainwaters may be encountered with ionic concentrations of the order of several thousand microequivalents per liter. Cation-anion balance may not give acceptable values for acidity of the initial rainfall in these cases as the total ion content is much higher than the H^+ concentration and relatively small analytical errors would drastically affect the estimated acidity. Unfortunately, when higher concentrations are present, direct pH measurements may also be a poor indicator of the effect of the water on the acid base relationships of the soil due to the increased probability of incomplete ionization of acids or bases.

In order to examine the validity of this relationship, two sets of data were selected from the literature and H^+ ion loading calculated by the anion minus cation method. The observed vs. predicted values were then compared by linear regression. For the data of Pearson and Fisher (1971), the relationship obtained using all 37 points was: $Y = 9.24 + .758\ X$ with a correlation coefficient (r) = .826; where Y is the observed H^+ minus HCO_3 in millimoles per square meter per year and X is the anions minus cations in milliequivalents per square meter. It was also noted that a good deal of the scatter resulted from a few coastal points where high Na^+ and Cl^- levels appeared to be erratic. When the coastal points were excluded the least squares regression equation for the remaining 30 observations was; $Y = 5.71 + 0.90\ X$ with a correlation coefficient (r) of 0.900. This relationship is shown in Figure 4.

A similar comparison was made using data given by Egner and Eriksson (1955b). In this case the least squares regression equation was $Y = 0.12 + 0.571\ X$ with a correlation coefficient (r) of 0.750; where Y is observed H^+ minus HCO_3^- and X is calculated from anions minus cations. Both X and Y are in units of milliequivalents per square meter for a one month period and n=43. One location extremely high in Na^+ and

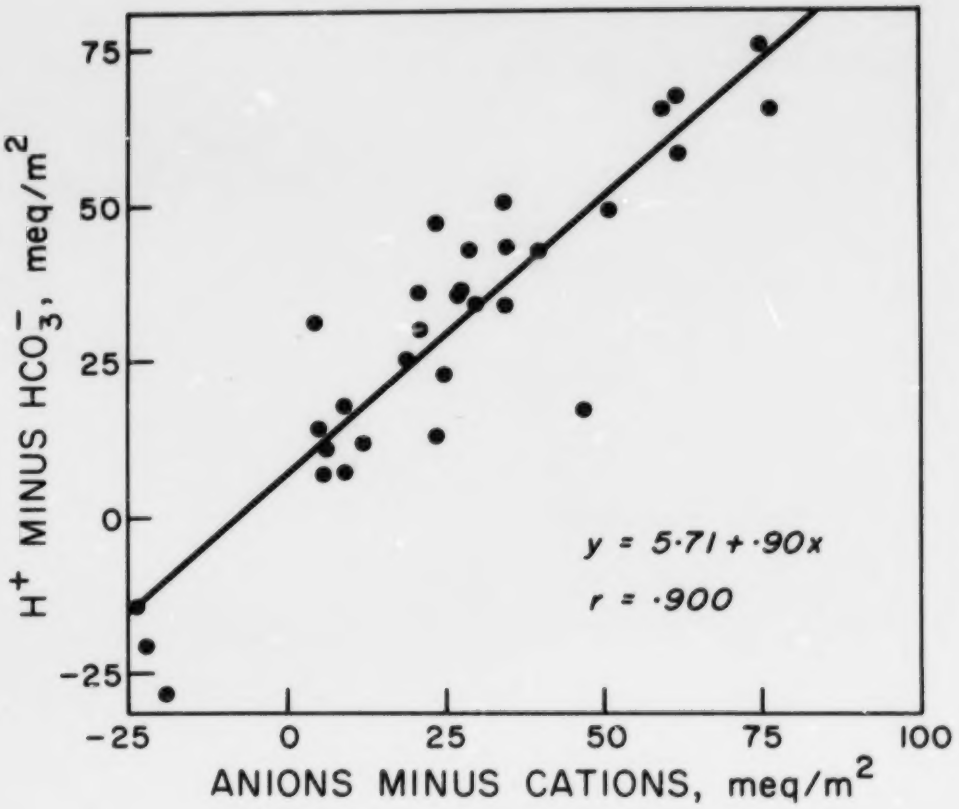

Figure 4 Relationships between net acidity as calculated by anions (excluding HCO_3^-) minus basic cations, and observed H^+ minus HCO_3^- for data set reported by Pearson and Fisher (1971). Coastal stations were not included.

Cl^- was excluded. The relationship is shown in Figure 5. This case is interesting because most of the values are negative, i.e. the samples were effectively basic. The bulk of the scatter appears to arise from the negative values. Whether this reflects analytical errors or is due to other causes is not known. It is entirely possible that the anion minus cation values more accurately reflect the net H^+ loading of the system than the H^+ minus HCO_3^- values.

Granat (1972) has proposed a model for calculating acidity of rainfall from the concentration of the individual ions as follows:

$$a = 2\left([SO_4^{2-}] - \frac{27.6}{457}[Na^+] + [NO_3^-] - [NH_4^+]\right) \quad (16)$$

$$b = \frac{1}{2}\left([K^+] - \frac{9.7}{457}[Na^+]\right) + \left([Mg^{2+}] - \frac{55.6}{457}[Na^+]\right) \quad (17)$$

$$+ \left([Ca^{2+}] - \frac{10.0}{457}[Na^+]\right) \quad (18)$$

$$e = a - 2b$$

Where: a = amount of available acid

b = amount of base expressed as moles of carbonate

e = excess acid in moles per liter (-e = alkalinity)

This model assumes that all sodium in rainfall is of marine origin. The fraction of the SO_4^{2-}, K^+, Mg^{2+}, and Ca^{2+} assumed to be of marine origin is equal to the concentration of sodium times the ratio of the respective ion in sea water to the concentration of sodium in sea water. The model is apparently intended to represent the net acidity or alkalinity of rainfall assuming it to be an aqueous solution or suspension formed from sea salts, sulfuric acid, nitric acid and

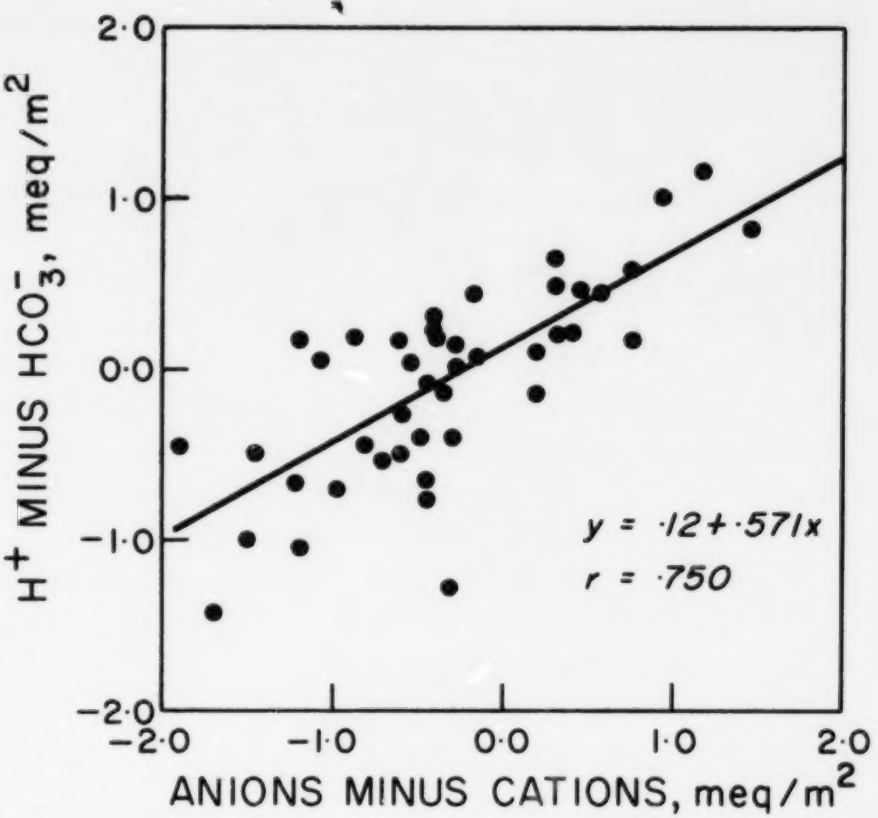

Figure 5 Relationship between net acidity as calculated by anions (excluding HCO_3^-) minus basic cations, and observed H^+ minus HCO_3^- for data set D502 reported by Egner and Eriksson (1955b). One coastal station not included.

ammonia. Implicit in the model is the assumption that the ratio of Cl^- to Na^+ is the same in rainfall as in sea water. Granat shows that the model is reasonably accurate in predicting the net acidity or alkalinity of rainfall.

It may not be readily apparent to the causual reader, but this model is actually a form of the strong acid anion minus basic cation method of calculating acidity shown in equation (15). The models are identical if the molar ratio of Cl^- to Na^+ in the rainfall is 1.19, the ratio found in sea water. Deviations of acidity or alkalinity calculated by Granat's model from measured values should be equal to the difference between measured Cl^- concentrations and an estimated Cl^- concentration determined by multiplying the Na^+ concentration by 1.19.

The concept of cation-anion balance and electrical neutrality of the system is also useful in considering acid-base relationships of plant uptake of ions. In order to maintain electrical neutrality in the system, the plant must either take up equal amounts of cations and anions on an equivalent basis or, if the amounts are unequal, it must release to the solution an amount of ions equal to the difference and of the same charge as the excess. A reasonable conceptual model of this effect is that the plant gives off H^+ ions equal to the excess of cations over anions taken up, and indeed this seems to be the case (Fried and Broeshart, 1967 p. 97). The converse of this is that an excess of uptake of anions over cations is balanced by a release of OH^- ions which appear in the media as HCO_3^- due to the presence of CO_2.

Most plants take up more anions than cations, but this may be reversed if the bulk of the nitrogen uptake occurs as NH_4^+ rather than NO_3^-. Variations of a magnitude sufficient to cause major differences in the acidity relationships of the media may occur. Healthy plants usually contain substantially lower quantities of the usual anions, i.e.

NO_3^-, Cl^-, SO_4^{2-}, and $H_2PO_4^-$, than of the basic cations. This results from the reduction of SO_4^{2-} and NO_3^- to reduced forms of S and N which are utilized in the protein structure. The excess of basic cations are electrically balanced by organic anions formed in the plant. During the breakdown of the dead plant material, these basic salts of organic acids may be hydrolyzed. The bases are removed and leached as bicarbonates and the remaining litter is acidic due to the presence of these organic acids. If the pH lowers to the point that bicarbonates can no longer exist, this mechanism of leaching is no longer operative. Bases than can only leach in conjunction with the above anions or by chelation with certain organic complexes.

The acid base relationship of this soil-plant system are complex. It does not seem justified to regard this in terms of a simple input-output system of H^+ ions; the cation-anion balance and acidity relationships of the whole soil-plant system must be considered. Apparently one critical research need, in terms of evaluating ecological effects of acid rainfall, is to synthesize present knowledge of the acidity and cation-anion relationships into an overall model from which testable hypotheses can be developed. Some important aspects of this system are considered in more detail in the following sections.

SECTION VI
ACIDITY RELATIONSHIPS OF THE SULFUR CYCLE

An important aspect of the acid rainfall problem concerns the possible effects of sulfur inputs from anthropogenic sources on soil-plant systems. Most papers seem to focus on the acidity of rainfall, presumably resulting from sulfuric acid formed by the oxidation of atmospheric sulfur dioxide. It would seem desirable to consider possible effects from the standpoint of the total sulfur cycle, rather than from a consideration of an isolated portion of the cycle. Thus a brief description of the acidity relationships of this cycle appears relevant and appropriate.

While sulfur may be present in a variety of forms in plant tissue and plant residues, it is mostly in reduced (S^{2-}) form. The bulk of the sulfur is found in the amino acid units of the various proteins. Micro-organisms that break down plant residue and soil organic matter may utilize directly the reduced sulfur in the organic material or, in some cases, may utilize sulfate sulfur from the surrounding media. At any rate, the organic sulfur compounds are transformed to reduced or incompletely oxidized forms such as sulfides, elemental S, thio-sulfates etc., (Starkey, 1966). These reduced or incompletely oxidized compounds are then apparently oxidized to sulfate by aerobic chemautotrophs in the soil. The oxidation of the reduced sulfur from plant material and soil organic matter to the sulfate form will inevitably be accompanied by the release of two H^+ ions for each sulfur atom oxidized. This general reaction may be represented by equations (19) and (20) for sulfide and elemental sulfur:

$$H_2S + 2\ O_2 \rightarrow 2H^+ + SO_4^{2-} \qquad (19)$$

$$S + 3/2\ O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-} \qquad (20)$$

Thus in Figure 6, the oxidation of organic sulfur to SO_4^{2-} is shown as releasing 2 H^+ ions. H_2S may also act as an acid, but the disassociation constants are such (pK_1 = 7.24, pK_2 = 14.92) that it would be largely non-ionized in acid soil systems.

If we assume the SO_4^{2-} released is rapidly taken up by plants, the acid formed by the oxidation will be balanced by the release of 2 OH^- (or HCO_3^-) ions from the plant in the uptake process (Figure 6). The net change in H^+ ions for the overall process in the soil is zero (2 H^+ and 2 OH^- ions formed), and no change in acidity results. The consideration of the OH^- ions released by the plant as a result of uptake of anions is an essential point. However, it cannot be validly considered in isolation, but must be considered as a part of the total cation-anion balance of nutrient uptake and plant processes.

Plants apparently take up sulfur almost entirely as the sulfate ion but, as noted previously, the preponderance of sulfur in the plant is in the reduced form. Sulfate is reduced to the S^{2-} form within the plant prior to its incorporation into the structure of the plant in forms such as the sulfur containing amino acids. This reduction results in the removal of 2 H^+ (Figure 6) ions according to a reaction that may be considered the reverse of (19) above. The consumption of 2 H^+ ions at this point balances the loss of 2 OH^- ions, (which may be considered as equivalent to formation of 2 H^+ ions) during the uptake of sulfur.

The total H^+ ion production and consumption of the sulfur cycle (Figure 6) is balanced and no net change in acidity should result. While the cycle represents a drastic simplification of the sulfur oxidation-reduction processes in the system, the acidity relationships should be basically valid.

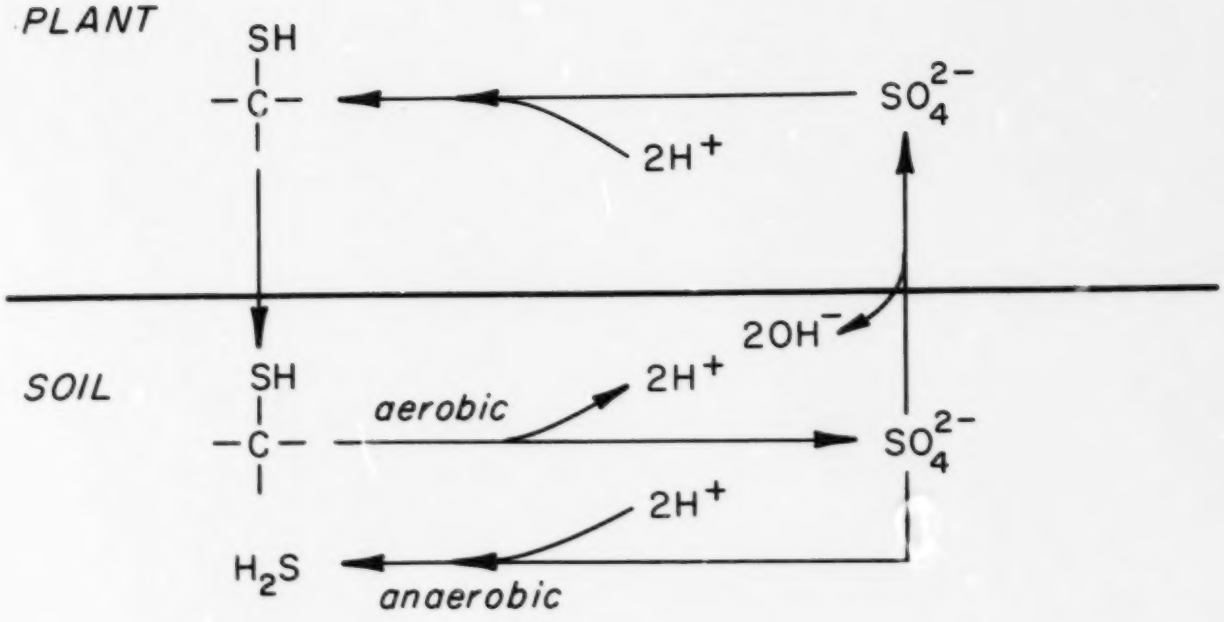

Figure 6 Simplified sulfur cycle showing acid formed or consumed by the various processes.

The anaerobic reduction of sulfate to sulfide (Figure 6) requires low oxygen levels and a fixed carbon energy source, as it is carried out by heterotrophic anaerobic organisms. High concentrations of sulfide compounds may accumulate in flooded soils where sulfate is continually replenished, such as river deltas. This process tends to produce neutral or basic soils as H^+ ions are consumed. Drainage of these soils results in rapid acidification due to H^+ produced during the oxidation of S^{2-} to SO_4^{2-}.

While the sulfur cycle is inherently balanced as far as acid production and consumption are concerned, it does provide some potential for leaching of bases and subsequent development of soil acidity. This arises because lags may occur between oxidation to sulfate and uptake of the sulfate ion. If sulfate ions accumulate, there is a concomittant increase in H^+ formed in the oxidation of reduced sulfur to sulfate. The H^+ ions replace basic cations on the clay and organic matter complexes, and these bases may be leached from the soil in association with the SO_4^{2-} anion. The quantification of any acceleration of this loss of cations that may be due to acid rainfall is a critical aspect of the assessment of possible ecological effects that may result. Complications arise in this quantification due to the inter-relationships between the nature of soil acidity and the process of sulfate adsorption in soils.

In neutral or acid soils sulfate ions may remain in the soil solution or become adsorbed on soil particles. Various conceptual models have been proposed but for our purposes it is most useful to consider this adsorption to be an anion exchange phenomenon. Soil particles are generally negatively charged but some positive charges exist as the result of the amphoteric nature of soil organic matter and broken bonds on the edges of the clay lattices. As soils become acid, the alumina silicates tend to decompose as represented by equations 21-23.

$$Al(OH)_3 + H^+ \leftrightarrow Al(OH)_2^+ + H_2O \quad (21)$$

$$Al(OH)_2^+ + H^+ \leftrightarrow Al(OH)^{2+} + H_2O \quad (22)$$

$$Al(OH)^{2+} + H^+ \leftrightarrow AL^{3+} + H_2O \quad (23)$$

According to this model most reserve acidity in soils does not consist of H^+ ions adsorbed on negatively charged soil colloids but exists in the form of monomeric Al^{3+} and positively charged hydroxy aluminum complexes and polymers. These positive charges neutralize negatively charged colloids or adsorbed anions such as SO_4^{2-}. As soils become more acid their cation exchange capacity decreases due to neutralization of negative charges by this mechanism. The increase in positive charges with acidification increases the capacity of soils to adsorb anions such as sulfate (Harward, Chao, and Fang, 1962; Harward and Reisenaur, 1966). Apparently as acidity increases due to anthropogenic sulfur inputs, the ability of the soil to hold the sulfate ion through the adsorption mechanism would also increase.

Recent data of Nyborg et. al., (1973) indicate that direct soil absorption of SO_2 may be substantial. Directly downwind from a source in central Alberta, they found enrichment in the range of 10-20 kilograms S per hectare over a three month period.

If reduced sulfur such as elemental S° is added to an aerobic soil system, we can expect oxidation to SO_4^{2-} by soil organisms and the concomitant release of H^+ ions. If acid rainfall containing H_2SO_4 enters the system, the H^+ ions are supplied directly. If the rainfall contains a mixture of H_2SO_4 and H_2SO_3 (Brosset, 1973), the pH of the rainfall would not be as low as for a similar concentration of H_2SO_4 alone, due to the lower dissociation of H_2SO_3. However, as soon as

temperature and moisture conditions become favorable, the SO_3^{2-} would undoubtedly be oxidized to SO_4^{2-} in the soil. Thus, the net effect on the acidity of the soil system would be the same of H_2SO_3 as for H_2SO_4.

From the above we see that the net increase in acidity per mole of sulfur added is identical for reduced sulfur, sulfuric acid or sulfurous acid. If acid rainfall containing H_2SO_4 enters the system, H^+ ions are supplied directly. The dissociation constants for H_2SO_3 are much lower, but added sulfite would be oxidized to sulfate assuming temperature and moisture levels are favorable. In all cases, the acidity is increased. However, if the SO_4^{2-} is rapidly absorbed by the plant systems, the resultant release of OH^- ions (Figure 6) would tend to balance the extra acidity.

Sulfur loads calculated from the data of Pearson and Fisher (1971) for the northeastern U.S., tend to be in the range of 8 to 15 kg ha^{-1} yr^{-1}. Jonsson and Sundberg (1970) give a value of 9 kg ha^{-1} yr^{-1} for the Swedish forests. Values of this magnitude could probably easily be absorbed by most agricultural ecosystems as they are in the same general range as harvest removals of sulfur. In forest ecosystems a long-term build up in soils, plants, and litter might be expected. If loading is greater than the capacity of the ecosystem to utilize or store sulfur, leaching losses will probably occur, bases will be lost in conjunction with the SO_4^{2-}, and the soil will become more acid.

The above discussion refers specifically to inputs of sulfur that are not balanced by basic cations. If rainfall inputs of sulfate are accompanied by similar amounts of basic cations, i.e., Na^+, Ca^{2+}, Mg^{2+}, or K^+, little change in soil acidity would be expected. Over long periods of time, however, if the distribution of these input ions is

different than the distribution of ions in the soil solution and in equilibrium with exchangeable cations in the soil, a shift in the cation equilibria could occur. The effect of such a shift would depend on the resultant distribution.

The capacity to utilize additional sulfur is often closely related to the nitrogen cycle. Nitrogen sulfur ratios of most plant proteins will be in the range of 12:1 to 16:1, while ratios in soil organic matter tend to be of the order of 8:1 or 10:1 (Stewart and Whitfield, 1965). When nitrogen being taken up by plants is largely derived from soil organic matter, the growth limiting nutrient is more likely to be nitrogen than sulfur. The sulfur mineralized will probably be sufficient for utilization of the nitrogen mineralized. However, if nitrogen comes from an outside source such as fixation of atmospheric nitrogen or non-sulfur containing fertilizers, the probability of sulfur deficiency is substantially increased. Thus sulfur responses in agriculture are generally found on legume crops such as alfalfa and clover or on crops where heavy nitrogen fertilizer applications are made using fertilizer materials that do not contain sulfur. In forest ecosystems where nitrogen fixation is rapid such as in alder stands, there is a definite possibility that anthropogenic sulfur inputs would result in accelerated growth. In such systems the removal of sulfur as a growth limiting factor would probably increase productivity. It is even possible that sulfuric acid in rainfall would not result in increased soil acidity due to the balancing effect of the OH^- ions given off by the plant in the uptake of SO_4^{2-}.

Mature timber stands or other systems in which nitrogen is supplied largely from internal cycling are less likely to be sulfur limited. If the capacity of these ecosystems to utilize sulfur inputs is exceeded, the probability of deleterious effects from sulfuric acid containing rainfall would be increased.

Finally, the effect of sulfur inputs on base rich soils should be considered. Such soils are generally found in arid areas, but occasionally occur under humid or subhumid conditions. These soils are virtually 100% base saturated, i.e., all cation exchange positions are occupied by bases, and they generally contain free alkaline earth carbonates. The acid-base relationships of the sulfur cycle here are identical to those discussed above except for the effect of excess acid. Free carbonates result in a large buffering capacity. Acid rainfall high in sulfate ion would dissolve the carbonates, and sulfates would tend to accumulate at some point in the profile and precipitate out as gypsum. This should not cause a problem as many soils naturally contain layers where free gypsum crystals are present. Sulfur bearing fuels might well be exhausted before large areas of soil carbonates are depleted. However, some ecological effects are possible as many calcareous grassland soils are actually acidic near the surface. Acid inputs from acid rainwash might be expected to intensify and extend this layer. While the process would probably be very slow, the long-term ecological consequences are unknown.

SECTION VII

ACID-BASE RELATIONSHIP OF THE NITROGEN CYCLE

In light of the recent interest in the effect of anthropogenic sulfur inputs on the acid-base relationship in soil-plant systems, it is appropriate to call attention to the role of the nitrogen system in this regard. From an overall ecosystem point of view, the nitrogen cycle can be expected to release or consume much greater quantities of H^+ ions than would be involved in the sulfur cycle. Also the contribution of nitrogen compounds to the potential of rainwater to acidify soil systems may be much greater than generally recognized. Plant uptake of nitrogen occurs in both the NH_4^+ and NO_3^- forms. Factors that determine the relative uptake in each of these forms include the nature of the plant and the presence or absence of conditions favorable to the oxidation of NH_4^+ to NO_3^- in the soil system.

While plants may contain many types of nitrogen compounds, the major portion of the nitrogen is found in the structural proteins. This nitrogen is in the N^{3-} oxidation state, the same as is found in NH_3, NH_4^+ and soil organic nitrogen. When plants take up nitrogen in the NH_4^+ form, no change in oxidation state in the system is required (Figure 7). Starting with the soil organic component in Figure 7, we consider the release of N to be a simple deamination of $-CNH_2$ to NH_3 with no change in acid-base status required. This NH_3 will, require 1 H^+ ion to ionize as NH_4^+, or if the process is considered to be a hydrolysis, one OH^- is formed (Equation 18).

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (24)$$

The uptake of NH_4^+ by a plant results in the release or exchange of an H^+ ion so the net change in acidity for the soil system is zero. If ammonification occurs without either uptake or oxidation to NO_3^- so that

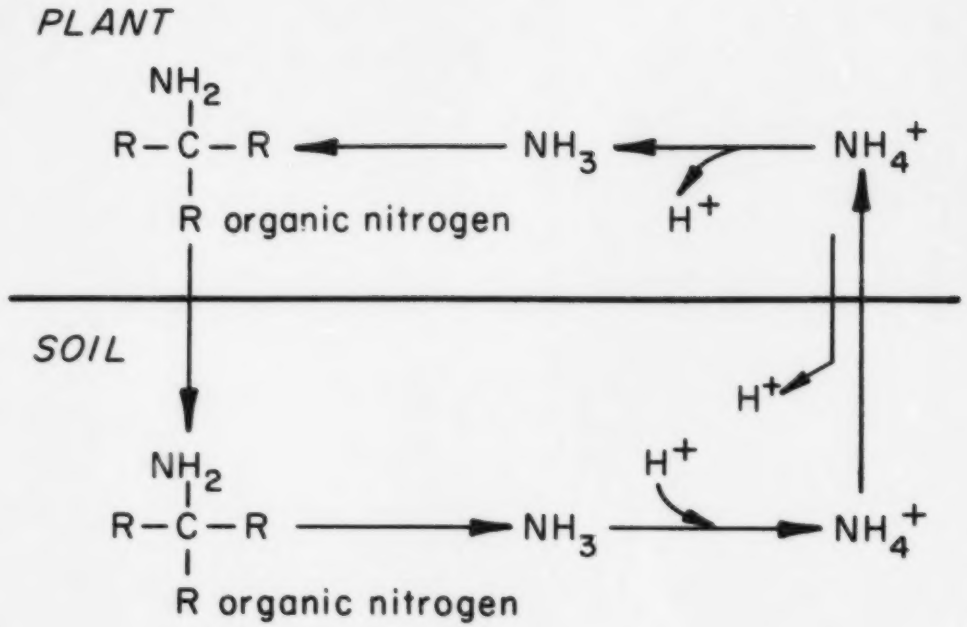

Figure 7 Simplified nitrogen cycle assuming all N utilized in the NH_4^+ form, and showing acid formed or consumed by the various processes.

NH_4^+ accumulates, we might expect the pH of the system to increase. This may occur but the relationship is complicated by the basic nature of the original $-NH_2$ group and by the formation of keto groups in the usual oxidative deamination. The acid-base relationships in the plant are relatively simple when nitrogen is taken up in the NH_4^+ form. One H^+ is released in the conversion to NH_3 or $C-NH_2$. This balances the H^+ ion released in the uptake process so the net change is again zero. The acid-base relationship of the cycle appears to balance as one would intuitively expect.

The system becomes more complex when we consider the oxidation of NH_4^+ to NO_3^- and the subsequent uptake of the nitrate ion (Figure 8). Starting again with the breakdown of soil organic matter, we represent the system as releasing NH_3. The subsequent protonation of NH_3 to form NH_4^+ requires 1 H^+ ion. The oxidation of NH_4^+ to NO_2^- and subsequently NO_3^-, releases a total of $2H^+$ ions, as shown below:

$$NH_4^+ + 3/2\ O_2 \rightarrow 2H^+ + NO_2^- + H_2O \qquad (25)$$

$$NO_2^- + 1/2\ O_2 \rightarrow NO_3^- \qquad (26)$$

$$NH_4^+ + 2\ O_2 \rightarrow 2H^+ + NO_3^- + H_2O \qquad (27)$$

These transformations are carried out in the soil largely by chemautotrophs, step (a) by organisms of the genus Nitrosammonas and (b) by Nitrobacter. The subsequent uptake of NO_3^- releases 1 OH^-, which balances one half the acidity released in the oxidation. The other half is balanced by the H^+ utilized in the protonation of NH_3. Again, we find the net change in the soil is zero and the system balances, provided the cycle is completed by plant uptake.

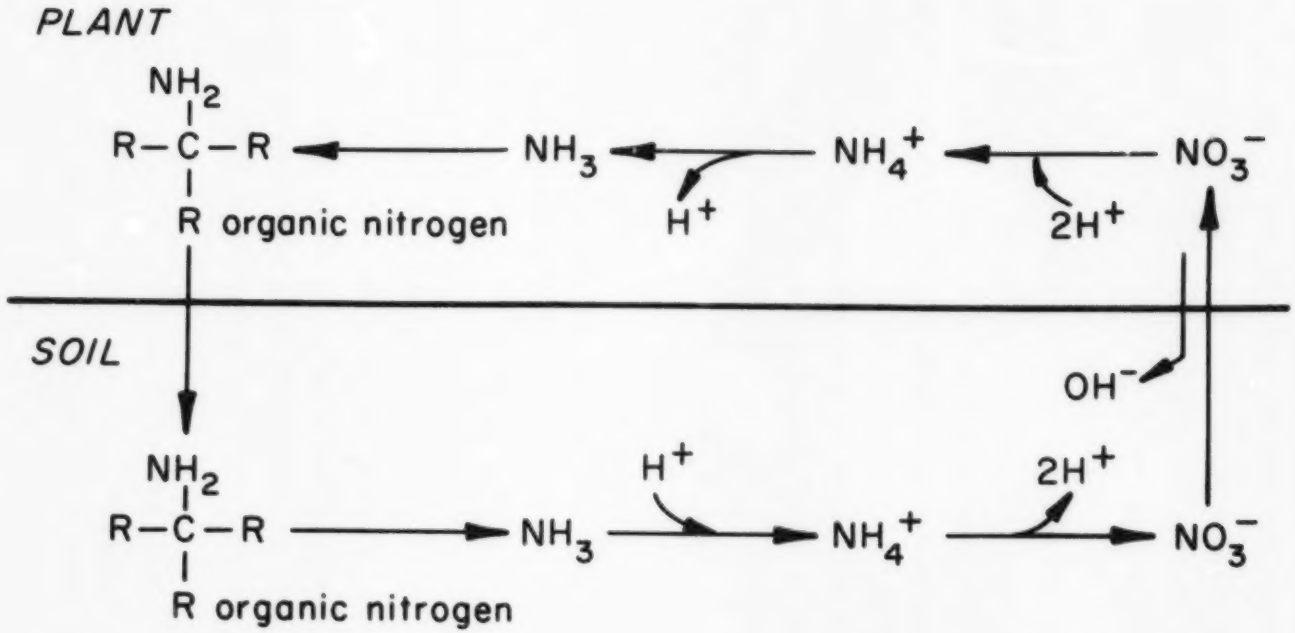

Figure 8 Simplified nitrogen cycle assuming all N utilized in the NO_3^- form, and showing acid formed or consumed by the various processes.

The plant transformations may be regarded as the reverse of those found in the soil. Two H^+ ions are consumed in the reduction of NO_3^- to NH_4^+ by the nitrate reductase enzyme system. One of these is balanced by the loss of an H^+ to form NH_3 prior to the amination. The other is balanced by the release of the OH^- that occurred during the uptake of NO_3^-, as an OH^- lost by the plant is equivalent to the formation of an H^+.

Even though the overall system can be considered balanced, the nitrogen cycle may, under certain conditions, offer potential mechanisms for losses of bases and subsequent acidification of the soil system. When mineralization occurs followed by the oxidation of NH_4^+ to nitrate, the H^+ ions formed will replace a basic cation on the cation exchange complex. This basic cation is then subject to leaching in conjunction with the NO_3^- ion. If conditions allow any build-up of NO_3^-, the potential for leaching exists when water passes through the profile. Most natural ecosystems tend to maintain low nitrate levels as the nitrates formed are rapidly taken up by the plants.

Some interesting questions arise when one considers the potential acidity relationships of mineral nitrogen inputs in precipitation. Any anion taken up by a plant will cause the release of an OH^- ion, so nitrate could be considered as resulting in a basic reaction. The highly mobile nitrate ion is rapidly absorbed by the plant, and Pearson and Fisher (1971) note that stream loads of mineral N are less than precipitation inputs. Even though this possible basic effect may be valid, one must be cautious in the interpretation of this effect in isolation from the rest of the cation-anion system.

Perhaps the most interesting aspect of the nitrogen cycle in relation to rainfall acidity involves the ammonium ion. If the NH_4^+ falling in precipitation is oxidized in the soil to the nitrate form,

2 moles of H^+ will be formed for each mole of NH_4^+ oxidized as shown by equation (27). The data of Pearson and Fisher (1971) show that this effect may be substantial. Table 1 shows values of the mean ionic concentration and loading for Mays Point, New York in 1966, calculated from their data. The NH_4^+ value of 15.1 milliequivalents of NH_4^+ per square meter at this location also happens to be the mean value for all locations and years that they report. At this location they report an H^+ loading of 34.9 milliequivalents per year which would correspond to a mean value of 44.8 microequivalents per liter with a total precipitation of 78 centimeters. This mean H^+ concentration results in an "average pH" of 4.35. If 2 moles of H^+ are released in the oxidation of each mole of NH_4^+ to NO_3^- (Equation 27), the oxidation of 15.1 milliequivalents of NH_4^+ to NO_3^- will result in the release of 30.2 milliequivalents of H^+ per square meter, an amount very similar to the 34.9 milliequivalents reported as the direct input from H^+ loading.

Another example of the possible significance of the effect of acidification due to oxidation of NH_4^+ can be seen from data shown by Likens (1972) and Likens and Bormann (1974). These authors call attention to an apparent shift from NH_4^+ to NO_3^- as the dominant form of inorganic nitrogen at Geneva and Ithaca, New York since about 1945. They also note increasing acidity of rainfall over the same period as evidenced by pH values of about 4.0 at present. No direct pH measurements are available for the early samples, but they are inferred to be higher due to the recorded presence of bicarbonates and from their reaction to methyl orange indicator. The data are presented in graphical form, but apparently a value of 0.9 milligrams NH_4^+ per liter is representative of the bulk of the observations prior to 1945, with a few values above 3.0. The release of 2 H^+ ions per mole on oxidation of 0.9 milligrams NH_4^+ per liter would release 0.106 milligrams H^+ per liter. This is almost identical to the H^+ concentrations shown by

Table 1. AVERAGE IONIC LOADING AND COMPOSITION FOR RAINWATER COLLECTED AT MAYS POINT, NEW YORK IN 1966 (PEARSON AND FISHER, 1971).*

Cations	Milligram Equivalents, $meter^{-2} \cdot year^{-1}$	Microgram Equivalents, $liter^{-1}$
Ca^{2+}	35.7	45.9
Mg^{2+}	11.7	15.0
Na^{+}	8.1	10.4
K^{+}	3.1	4.0
NH_4^{+}	15.1	19.4
H^{+}	34.9	44.8
Anions		
SO_4^{2-}	87.9	113.0
Cl^{-}	10.5	13.5
NO_3^{-}	2.7	3.5

*Data as shown by Pearson and Fisher was in units of tons per square mile per day. Precipitation totaled 78 centimeters.

Likens (1972) for six collection stations near Ithaca, New York in 1970-71. This, of course, may not infer that if oxidation of the NH_4^+ in these early samples had occurred, the H^+ concentration would have been 0.106 milligrams per liter (pH = 3.98) as the buffering effects of bicarbonates in the system cannot be estimated. However, a consideration of the acidification potential of the ammonium present may well modify substantially our conclusions concerning the relative acidification effects of the early rainwater samples as compared to present day "acid rainfall."

It is also important to recognize that the oxidation of NH_4^+ to NO_3^- by aerobic chemautotrophs may occur in rainfall collection vessels unless appropriate precautions are taken. If this occurs acidification results. We can see by the above examples that the potential increase in observed acidity could be significant; in the case shown in Table 1, for instance, the oxidation of the NH_4^+ to NO_3^- would drop the "average pH" from 4.35 to 4.03, nearly doubling the H^+ loading as usually calculated from pH measurements. Serious questions about the validity of many pH measurements of rainfall samples might be appropriate on this account.

One could argue that the appropriate pH would be that taken after oxidation occurs, as the acidification effect will be manifested when the oxidation occurs in the soil. This has the disadvantage of ignoring the acid-base relationships of the nitrogen uptake processes. We seem to be forced to conclude that the acidification effects of rainfall are closely linked to other ecosystem processes, particularly those of the nitrogen cycle. Consideration of the acidity of rainfall in isolation may be an unwarranted oversimplification.

When ammonium is taken up directly by the plant, acidification still occurs due to the H^+ given off by the plant in the uptake process. The magnitude of this effect is often underestimated. In the past many

experiments showing poor growth in solution and pot cultures when ammonium was used as a nitrogen source were interpreted as a toxic effect of NH_4^+ ion when in fact the toxicity was caused by acidity developed in the medium. Carnation producers had long considered NH_4^+ as an unsuitable source of nitrogen, but it has been shown that they do well when NH_4^+ is used if $CaCO_3$ is added to prevent acidification (Schekel, 1971).

Ammonium inputs, whether oxidized to nitrate or not, can thus be shown to have an acidifying effect. While it is probably extreme to consider the total potential acidification as representing two moles H^+ per mole of NH_4^+, the effect should be recognized in our evaluation of the effect of rainfall acidity.

If ammonium inputs are important, it may be well to consider their source and distribution. In past years, many measurements of nitrogen inputs in rainfall were made for the purpose of evaluating their agricultural significance. Results vary widely, and it is impossible to accurately evaluate whether the variation is due to contamination and analytical inaccuracies or actual variation in amounts. It has been noted that the results quite consistently show a 2:1 ratio of ammonium to nitrate N (Stevenson, 1965), but the results of Pearsons and Fisher (1971) show widely varying ratios both between locations and between years at a single location.

Atmospheric ammonia levels vary widely. Sources of ammonia often widely quoted include industrial, atmospheric fixation (electrical and photochemical), and volatilization from land surfaces. Recently Luebs, Davis, and Laag (1973) have shown much higher atmospheric concentrations of NH_3 in a dairy area in California than in a control area. They also claimed NH_H^+ inputs in the precipitation in the dairy area to be three times that of the control area. Hutchinson and Viets (1969) have

reported high ammonia absorption by traps near feedlot operations. Thus, the possible effects of high concentrations of livestock must be considered as well.

Atmospheric NH_3 reacting with sulfuric acid aerosols would form ammonium sulfate and bisulfate salts as shown in Equations (28) and (29).

$$H_2SO_4 + NH_3 \rightarrow NH_4^+HSO_4 \quad (28)$$

$$NH_4^+HSO_4 + NH_3 \rightarrow (NH_4^+)_2\ SO_4 \quad (29)$$

The resultant solution would be much less acidic than aerosols not neutralized by NH_3, yet the system would retain the capacity to acidify soils as shown by the mechanisms discussed above. Therefore, the neutralization of acid aerosols by atmospheric NH_3 may not reduce the capacity of the rainfall to acidify soils.

In conclusion, it probably is not possible at the present time to predict quantitatively the effect of nitrate and ammonium on the capacity of acid rainfall to acidify the soil system. On theoretical grounds we could expect substantial effects, and evaluation of this contribution should be included among the goals of future research on the acid rainfall problem.

SECTION VIII

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